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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

THE UNIVERSALLY EXACT APPLICATION OF FARADAY'S LAW.*

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Presented by T. W. Richards, November 12, 1902. Received October 9, 1902.

RECENTLY it has been shown † in this Laboratory that Faraday's Law holds with great precision at ordinary temperatures in aqueous solutions, for the two metals silver and copper. The long series of experiments, with probable errors of less than one in twenty thousand, yielded a ratio of the electrochemical equivalents equalling the ratio of the chemical atomic weights, within this small range of error.

While this was indeed but the comparison of a single pair of elements, it seems, nevertheless, safe to conclude that when side-reactions are wholly eliminated all other cases of comparison in aqueous solution would yield similar results. The experiments in question do not in the least serve to show that the law is independent of the nature of the solvent or the temperature, however. In attempting to probe into the meaning of this fundamental law, definite knowledge concerning these conditions is necessary; hence, new experiments at high temperature and with different solvents seemed highly desirable.

It will be remembered that approximate experiments at high temperatures and with other solvents have already been made by several experimenters; ‡ and there could have been no doubt as to the *approximate* fulfilment of the law under widely varying conditions. But none of these series of experiments yielded results trustworthy within one part in a thousand, and most of them showed deviations of at least one per cent; hence the possibility of slight deviations remained open.

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* A preliminary announcement of this work was made at the meeting of the Am. Asso. Adv. Sci. at Pittsburg in July, 1902, and an abstract was published in "Science" (N. S.) **16**, 284 (1902).

† Richards, Collins, and Heimrod, These Proceedings, **35**, 123 (1899); Richards and Heimrod, ibid., **37**, 415 (1902); also Zeitschr. phys. Chem., **32**, 321 (1900), **41**, 302 (1902).

‡ Faraday; see Ostwald, Electrochemie, 520; Kahlenberg, J. Phys. Chem., **4**, 349 (1900); Merrill, Phys. Rev., **10**, 169 (1900); Helfenstein, Z. anorg. Chem., **23**, 255 (1900).

In the experiments which are described below, a single metal, silver, was deposited in two successive, widely different cells by the same current. The conditions were so chosen as to make possible the elimination or determination of all conceivable side-reactions.

One of the cells consisted simply in the porous cup voltameter, or coulometer, which has been shown to give consistent and accurate results.* The other was a precisely similar arrangement of apparatus filled with a solution of argentic nitrate in fused potassic and sodic nitrates, maintained at about 250°.

This mixture of nitrates has a double advantage over pure argentic nitrate as an electrolyte. In the first place, the comparatively small concentration of silver diminishes the danger of accidental reduction, and in the next place, the foreign solvent enables one to determine the amount of mother liquor included in the crystals. The solution-tensions of the alkali metals are so high as to prohibit the electrolytic deposition of a weighable trace of either in the presence of an excess of dissolved silver.

It is true that this plan of experiment introduced two variables at once into the problem, a proceeding logically incomplete. If a difference were found between the two deposits of silver, further experiments would be needed in order to determine if this difference were due to the change of solvent or to the change of temperature. Such further experiments would have been made if they had seemed necessary; but the chances against accidental coincidence seemed so great as to eliminate any serious danger from the interpretation given below. This is fortunate, for it is not easy to find a single solvent capable of yielding satisfactory results over so large a range of temperature.

Although all three nitrates were prepared in a state of great purity by known methods, it was found very difficult to obtain fused solutions free from a slight precipitate of reduced silver. Hence, in order to avoid danger of error from this source, the fused mixture was filtered by its own gravity through an asbestos mat in a Gooch crucible, the whole apparatus being heated to 250° in a clean air-bath. Thus may be obtained a limpid and colorless fused mixture, which was used immediately for the electrolysis, being maintained at the high temperature with the help of a suitably arranged alcohol lamp. Great care was exercised to prevent the possibility of electrical leakage, the connections being made by carefully insulated air lines.

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* Richards and Heimrod, loc. cit.

When a first crude experiment had shown the feasibility of the arrangement, three more careful preliminary experiments were made. After the completion of each allotted time, the current of 0.2 ampere was broken, the two porous cups removed, and the two electrolytes decanted. Each cathode-crucible was thoroughly rinsed and allowed to stand for fifteen to eighteen hours in water. Two more washings with water, two with alcohol, and a thorough drying at 160° C. completed the treatment. In those cases when a trace of metallic silver was found in the decanted liquid, this trace was carefully collected on a Gooch crucible, thoroughly washed, and weighed. It was noted that the uppermost crystals deposited at the higher temperature were somewhat larger than the others, and also that no "anode dust" formed at 250°. The first of these facts may be ascribed to local action, due to slight thermal inconstancy [*] while the second is probably due to the rapid adjustment of equilibrium at the high temperature. Thus the chemical explanation given by Richards and Heimrod [†] of the appearance of the "anode dust" in aqueous solutions is supported; for if the anode dust were due solely to the mechanical detaching of bits of silver, there is no obvious reason why this process should not occur at high temperatures as well as at low temperatures.

Since all crystals formed from solutions contain included mother liquor, concealed in inaccessible cells, [‡] the silver which had been deposited from the molten solution was now examined for included sodic and potassic nitrates by dissolving it in pure nitric acid, precipitating the silver by hydric sulphide, evaporating the filtrate, dissolving and filtering the residue, drying once more, and finally weighing. Hydric sulphide was used in order that platinum vessels might be employed throughout. The mother liquor included in the crystals deposited from aqueous solution was assumed to be 0.016 per cent, the average of many determinations. [§]

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[*] Gladstone and Tribe (Phil. Mag.), (5) **11**, 508.

[†] These Proceedings, **37**, 428 (1902).

[‡] The effect of such inclusion is particularly obvious in the work of Merrill already quoted.

[§] Richards and Heimrod, These Proceedings, **37**, 441.

PRELIMINARY COMPARISON.

	Silver deposited at 250°.			Silver deposited at 20°.		Difference.	
	Observed.	Impurity.	Corrected.	Observed.	Corrected.	mg.	per cent.
	grams.	m.g.	grams.	grams.	grams.		
2	0.5761	0.4	0.5757	0.5758	0.5757	0.0	0.00
3	0.5942	0.2	0.5940	0.5739	0.5738	0.2	0.03
4	1.1729	1.1	1.1718	1.1720	1.1718	0.0	0.00
			Average				0.01

According to these preliminary results the varying conditions seemed to affect the weight of silver by only one part in ten thousand, the higher temperature yielding this slight excess of weight.

It became now a matter of interest to determine if this slight difference might be yet further reduced by the employment of yet greater care. Accordingly three much more accurate experiments were made, in a large dark-room which was for the time devoted wholly to this work. No injurious gases were allowed in the vicinity, and dust was as much as possible excluded. The current of 0.2 ampere was open for nearly two hours in each experiment. The impurity included in the crystals was more carefully determined in every case, the deposit from the aqueous solution being ignited at a dull red heat, while the alkali nitrate residues were converted wholly into sulphate, and freed from a last trace of silver by means of hydrochloric acid. The final dried residues of mixed sulphates weighed respectively 0.30, 0.54, and 0.32 milligrams. Since the nitrates of sodium and potassium were present in molecular proportions, and since the hot mother liquor contained ten per cent of argentic nitrate, these values correspond to corrections of 0.39, 0.69, and 0.42 milligrams respectively — corrections which are applied below.

The mother liquor included in the silver formed in the cool cell must also have contained dissolved argentic nitrate to the extent of about 0.02 milligrams in each case, an unimportant amount which is nevertheless subtracted below for the sake of completeness.

All weighings were made by substitution on a very precise balance with weights carefully corrected; and in general all the precautions needed in work upon atomic weights were observed.

The final figures thus obtained are as follows: —

FINAL COMPARISON.

Silver deposited at 250°.		Silver deposited at 20°.	Difference.	
Observed.	Corrected.	Corrected.	mg.	per cent.
grams.	grams.	grams.		
1.14958	1.14919	1.14916	0.03	0.003
1.12264	1.12195	1.12185	0.10	0.009
1.10242	1.10200	1.10198	0.02	0.002
Average				0.005

The largest difference is thus one tenth of a milligram, an amount not much greater than the possible experimental error, while the average difference has sunk to one in twenty thousand. It may be noted that of the six experiments, preliminary and final, four show no significant difference at all. The decreasing average difference with increasing care suggests that the slightly larger weights of silver obtained from the fused salt might be due to reduction of silver by organic dust, which it is difficult wholly to exclude. But even without this explanation, the results are close enough for present purposes, because an accuracy greater than one part in twenty thousand is rarely attained in other physicochemical measurement at the present time.

Summary.

In this paper it is shown that a galvanic current deposits essentially the same amount of silver from a solution of argentic nitrate in other nitrates at 250° as it does from an aqueous solution at 20°, within 0.005 per cent. Taken in connection with the previous work of Richards, Collins, and Heimrod, this result shows that Faraday's law is not a mere approximation, but is rather to be ranked among the most precise and general of the laws of nature.